A STUDY OF THE DISSOCIATING POWERS OF FREE AND OF COMBINED WATER

DISSERTATION

Submitted to the Board of University Studies of The Johns Hopkins University in Conformity with the Requirements for the Degree of Doctor of Philosophy.

by

G. FRED ORDEMAN.

1916.

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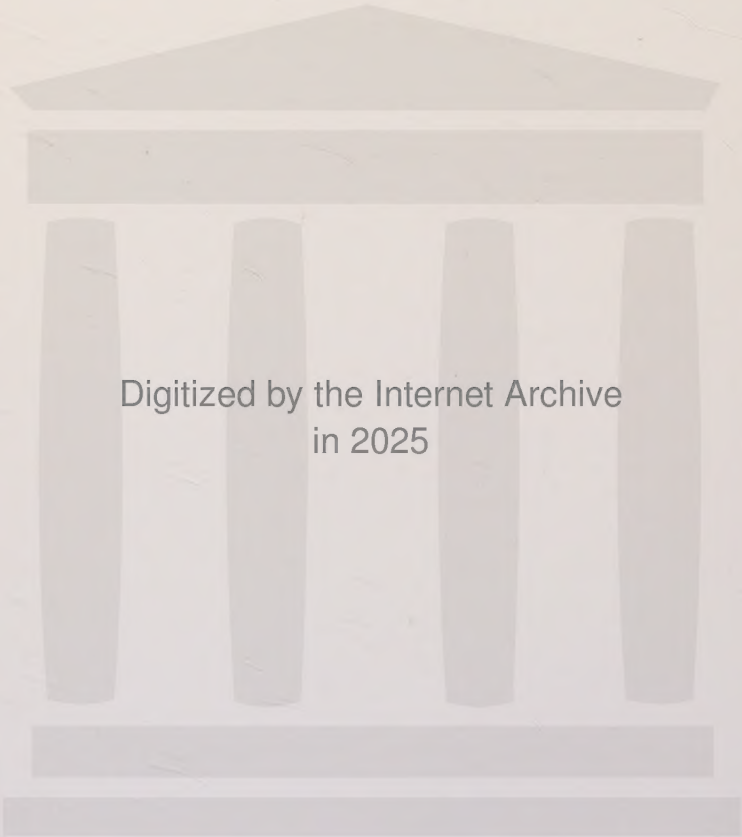
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TABLE OF CONTENTS

Acknowledgment 4

Introduction 5

Experimental 7

Apparatus 7

Solvents 9

Salts 12

Solutions 12

Procedure 14

Results 15

Discussion of Results 21

Biography 24

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The author gladly avails himself of this opportunity to express his sincere thanks to Professor Remsen, Professor Morse, Associate Professor Lovelace, Associate Professor Frazer, Associate Professor Reid, and Collegiate Professor Swartz for valuable instruction received both in the lecture room and in the laboratory.

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A STUDY OF THE DISSOCIATING POWERS OF FREE AND OF COMBINED WATER

INTRODUCTION

Jones and Uhler[1], Jones and Anderson[2] and Jones and Strong[3] during a period of five years studied the absorption spectra of solutions by the use of a vertical grating spectrograph. The various spectra were photographed and in this way the positions of the different absorption lines and bands were determined. They found that the solvent, the temperature and the concentration had a marked influence on the absorption spectra of salt solutions. Their results are best interpreted by the solvate theory, in which a distinction is made between water of hydration, if water is the solvent, and free or uncombined water.

One of the most interesting and important results established by Jones and Guy[4] in their quantitative study with the radiomicrometer on the absorption spectra of solutions, is the effect of the dissolved substance on the absorption spectra of solutions. They noted that aqueous solutions of hydrated salts are often more transparent than pure water. The absorption by aqueous solutions of strongly hydrated salts was compared by them

1 Carnegie Inst. Wash. Pub. No 60, p. 160 (1907); Amer. Chem. Journ., **37,** 126, 207 (1907).

2 Carnegie Inst. Wash. Pub. No. 110 (1909); Amer. Chem. Journ., **41,** 163, 276 (1909).

3 Carnegie Inst. Wash. Pub. No. 130 (1910); No. 160 (1911); Amer. Chem. Journ., **43,** 37, 97 (1910); **45,** 1, 113 (1911); **47,** 27, 126 (1912).

4 Carnegie Inst. Wash. Pub. No. 190 (1913); Amer. Chem. Journ., **49,** 1 (1913).

with the absorption by layers of water equal in depth to the water in the solutions. The concentrated solutions of strongly hydrated salts, e. g., 5.3 molar solution of calcium chloride, were found to be more transparent than a comparable quantity of pure water. In the case cited, the transparency was 25 per cent. greater from 1.05 μ to 1.2 μ. Similar experiments were carried out with salts which were but slightly hydrated. The solutions of these salts e. g., potassium chloride, ammonium chloride and ammonium nitrate, were found to have in general the same absorption as a layer of water of the same depth as the water in the solution. To account for such facts, they concluded that the combined water possesses less power to absorb light than free or uncombined water. They regard this as striking evidence that some of the water in the presence of salts which by other means are shown to hydrate, is different from pure, free, uncombined water. The simplest explanation seems to be that this is combined water or water of hydration.

The work of Jones and Guy has been repeated and extended by Jones, Shaeffer and Paulus.[5] Their results are of the same general character. In some instances they found the aqueous solutions of hydrated salts to be 40 per cent. more transparent than a comparable quantity of pure water.

It was believed that a determination of the power of dissociation of combined water might lead to the establishment of further differences between it and free water. With this in view Dr. Shaeffer suggested the use of isohydric solutions in the manner which has been adopted.

The object, then, of this work has been to ascertain the difference, if there be any, between the dissociating power of combined water or water of hydration and the dissociating power of uncombined or free water.

5 Carnegie Inst. Wash. Pub. No. 210, p. 9 (1915).

EXPERIMENTAL

APPARATUS

Conductivity Apparatus. The improved slide-wire bridge used for the conductivity measurements was made by The Leeds and Northrop Company, of Philadelphia. In this instrument the resistance wire, five meters in length, is wrapped around a marble drum. Readings were made corresponding in most cases to at least one-fourth of a millimeter. The resistance box had been standardized by the Bureau of Standards, Washington, D. C. An alternating current was supplied by an induction coil specially constructed for such work. The coil was actuated by a single lead accumulator and the strength of the current was regulated by adjusting the length of a thin manganin wire inserted between battery and coil. A telephone receiver was employed to determine the point of equilibrium. A double system of wiring was used between the rheostat, bridge and cell. Thus by means of a rocking commutator with mercury contacts, the positions of rheostat and cell relative to the bridge could be interchanged so that both "a" and "b" could be read directly. All copper wire in the external circuit was of such a gauge that the resistance was negligible. All connections were soldered.

Cells. Because of the high resistance of the water used a special "water cell," having large electrodes was necessary. The electrodes consist of two concentric platinum cylinders held in position by small drops of fusion glass in such a manner that they are about a millimeter apart. A fuller description may be found elsewhere.[6]

6 Carnegie Inst. Wash. Pub. No. 180, p. 89 (1913); Amer. Chem. Journ., **45,** 282 (1911).

Because of the large conductivity of the solutions measured a different type of cell was demanded. The cell which was finally adopted for this work has been previously used in this laboratory[7] for measurements of the conductivity of concentrated solutions. The U-shaped tube was made of difficultly soluble glass and was fitted with ground glass stoppers. A glass tube carrying a small platinum electrode is sealed by means of sealing wax into the hole bored in the center of each stopper. The tubes were first held in position by tamping wet asbestos between them and the walls of the stoppers. The distance between the electrodes can be changed by removing the wax, adjusting the tubes and resealing. The platinum plates are coated with platinum black. Numbers are etched upon the stoppers and the corresponding arms of the U-tubes so that the electrodes will always be placed in the same U-tube and in the same position.

Constant Temperature Bath. A constant temperature was maintained by the application of a principle most clearly stated by Morse:[8]

"If all the water or air in a bath is made to pass rapidly (1) over a continuously cooled surface which is capable of reducing the temperature slightly below that which it is desired to maintain, then (2) over a heated surface which is more efficient than the cooled one but which is under the control of a thermostat, and (3) again over the cooled surface, etc., it should be practicable to maintain in the bath any temperature for which the thermostat is set, and the constancy of the temperature should depend only on the sensitiveness of the thermostat and the rate of flow of the water or air."

The bath used is fully described by Davis and Putnam.[9] The "cooling surface" is a spiral-shaped copper tube

7 Zeit. physik. Chem., **49,** 389 (1904)
8 Carnegie Inst. Wash. Pub. No. 198, p. 56 (1914).
9 Carnegie Inst. Wash. Pub. No. 210, p. 119 (1915).

through which hydrant water is passed under a constant pressure. The pressure is maintained by a standpipe. The "heating surface" is a small part of a]-shaped heavy iron pipe against which a small gas flame is played. By means of an improved toluene-mercury thermo-regulator[10] and an electrically controlled gas regulator[11] the temperature was maintained constant to within 0.01°. The circulation of water over the cooling and heating surfaces is effected by means of a rapidly rotating propeller placed just inside the spiral copper tube. The propeller is driven by a 1-12 horse-power direct current motor and the power is transmitted by a belt drive.

A Beckmann thermometer graduated to 0.05° was used in the bath. Comparison was made with a thermometer recently sandardized at the Bureau of Standards, Washington, D. C.

Glassware. Measuring flasks, burettes and pipettes were recalibrated by direct weighing. Jena glass bottles were used for keeping the solutions.

SOLVENTS

Water. The water was purified by the method of Jones and Mackay[12] as modified by Schmidt,[13] and had a mean specific conductivity of 1.8×10^{-6} at 25° C.

Isohydric Solutions. If two solutions of electrolytes are mixed the conductivity of the mixture is, in general, less than the mean of the conductivities of the constituents. If the two solutions contain a common ion, however, there are concentrations at which they can be mixed without affecting each other's conductivity. This fact was first explained by Arrheinus.[14] He showed that if

10 Carnegie Inst. Wash. Pub. No. 230, p. 13 (1915).
11 Carnegie Inst. Wash. Pub. No. 210, p. 121 (1915).
12 Amer. Chem. Journ., **19,** 90 (1897).
13 Carnegie Inst. Wash. Pub. No. 180, p. 135 (1913).
14 Wied. Ann., **30,** 51 (1887).

equal volumes of two solutions of acids of certain concentrations be mixed, the conductivity of the mixture is the mean of the conductivities of the solutions, provided there be no appreciable change in volume. Such solutions are said to be *isohydric.* Arrhenius[15] defines them as follows:

"Two solutions of acids are isohydric whose conductivity, or in other words, whose electrolytic dissociation is not changed if they are mixed."

Arrhenius worked out the condition for two solutions containing a common ion to be isohydric, and has expressed it thus:

$$\frac{m\,\alpha}{v_1} = \frac{n\,\beta}{v_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

In this equation α = percentage dissociation of the salt in solution, v_1 = number of liters of solution containing a gram molecular weight of the salt, and m = number of common ions in each molecule of the salt. β, v_2 and n are the respective symbols for the second solution.

It was further shown by Arrhenius that two acids are isohydric if in a unit volume they contain the same number of hydrogen ions. With this principle in mind the investigator, in the course of his work, determined the concentrations of five different pairs of salt solutions when they fulfill the condition of being isohydric. This method follows.

In calculating the percentage dissociation by the conductivity method,—

$$\alpha = \frac{\mu_1}{\mu_1\,\infty} \qquad \beta = \frac{\mu_2}{\mu_2\,\infty} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Here μ_1 and μ_2 = molecular conductivities of the two solutions, $\mu_1\infty$ and $\mu_2\infty$ = the conductivities at infinite dilution.

15 Zeit. physik. Chem., **2**, 284 (1888).

From the method of Kohlrausch for calculating conductivity,—

$$\mu_1 = k_1 \frac{a_1 v_1}{b_1 w_1} \qquad \mu_2 = k_2 \frac{a_2 v_2}{b_2 w_2} \quad \ldots\ldots\ldots\ldots \quad (3)$$

k_1 and k_2 are cell constants. a_1, b_1, and a_2 and b_2 are the respective readings on the bridge for the resistances w_1 and w_2.

Substituting the values of (3) in (2), we obtain,—

$$\alpha = \frac{k_1 a_1 b_1}{b_1 w_1 \mu_1 \infty} \qquad \beta = \frac{k_2 a_2 v_2}{b_2 w_2 \mu_2 \infty} \quad \ldots\ldots\ldots\ldots \quad (4)$$

Substituting now the values of (4) in (1),—

$$\frac{m\ k_1 a_1 v_1}{b_1 w_1 \mu_1 \infty\ v_1} = \frac{n\ k_2 a_2 v_2}{b_2 w_2 \mu_2 \infty v_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

If the same cell be used in determining the conductivities of the two solutions, then, k_1 equals k_2 and simplifying (5) we obtain,—

$$\frac{m\ a_1}{b_1 w_1 \mu_1 \infty} = \frac{n\ a_2}{b_2 w_2 \mu_2 \infty} \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

This is the general equation which becomes further simplified for a particular case. A single illustration will make its meaning clear.

What concentration is necessary for a calcium nitrate solution that it be isohydric with regard to a molar solution of potassium nitrate? At 25° C., and this temperature was used throughout the work, for calcium nitrate, $\mu_1\infty$ equals 242.7,[16] and for potassium nitrate, $\mu_2\infty$ equals 139.6. Considering the nitrate ion, $m = 2$ and $n = 1$.

16 All $\mu\infty$ values were taken from Carnegie Inst. Wash. Pub. No. 170 (1912).

Therefore,—

$$\frac{2\ a_1}{242.7\ b_1w_1} = \frac{a_2}{139.6\ b_2w_2}$$

Whence,—

$$\frac{a_1}{b_1w_1} = .8693\ \frac{a_2}{b_2w_2}$$

Now by measuring a and b of the molar solution of potassium nitrate for the resistance w_2, the right hand side of the equation becomes a constant. A concentrated solution of calcium nitrate was taken in different portions and diluted until, by trial, that concentration was found such that $\frac{a_1}{b_1w_1}$ became equal to the value for the right hand side of the equation.

The concentration of the calcium nitrate was found to be .698 molar. And so a calcium nitrate solution of this concentration contains the same number of nitrate ions per unit volume as a molar solution of potassium nitrate.

SALTS

The majority of the salts used were the purest obtainable from Kahlbaum. All the non-hydrated salts were thoroughly dried at the temperature best suited to each salt. The hydrated salts, being so soluble, were in most cases not recrystallized but dissolved in conductivity water, filtered and used as concentrated solutions.

SOLUTIONS

Solutions for the first three salts in Table I were made as follows. Quantities of the isohydric solutions of the

two chlorides were made. The amount of added salt necessary for each concentration was weighed upon a watch glass and introduced into a calibrated flask through a short stemmed funnel. The salt was dissolved by one of the isohydric solutions and the flask placed in the bath regulated for 25° C. When the solution had come to a temperature it was diluted to the mark with more of the isohydric solution. The process was now repeated using the same flask and the other isohydric solution. But it was found that the volume change caused by the added salts was considerable. This means that the solutions when made would be of the proper strength for the added salt but weaker for the isohydric solutions. The results are, however, still comparable, as the volume change in the two isohydric solutions was found to be about the same.

Solutions for the other three salts in Table I were made in a different manner. Instead of using the stock isohydric solutions, they were made up as needed. The amount of potassium chloride necessary to make the isohydric solution molar, was weighed into the flask. The added salt being a hydrated one could not be weighed directly. It was added in the form of a concentrated solution of known strength from a small burette. The solutions were finally brought to the mark with conductivity water. For a comparable solution the necessary number of cubic centimeters of a concentrated calcium chloride solution of known strength, to make the solution .6951 molar, was used in place of potassium chloride. In this way solutions were obtained accurate with respect to the isohydric solutions but not with regard to the added salt because of the errors due to improper drainage of concentrated solutions in a burette of such small bore.

It was finally decided to take the densities of the various concentrated solutions and to add these solutions by weight rather than by volume. The densities were taken with a pycnometer. The solutions were added to the

weighed flasks (capacity 25 c.c.) from a burette with a finely drawn tip. With care the solutions could be weighed to within one or two milligrams, and this proved to be the most accurate method of handling these salts. As before, the same flask was used for comparable solutions and the possibility of errors was thus, in part, avoided.

The strengths of the different concentrated solutions of chlorides were determined by an estimation of the chlorine as silver chloride. The other concentrated solutions were analyzed for the cations. All solutions were made up at 25° C.

PROCEDURE

Six U-shaped cells were used in this work. Five of them had constants in the neighborhood of 14,000 while the sixth cell had a constant of 29,941. The constants were determined by means of a half-molar solution of potassium chloride. The molecular conductivity of this solution was found to be 108.85 (Siemens units) at 25° C.

Two solutions were first made isohydric by the means described above. The specific conductivities of these solutions were measured by the usual method and calculated from the formula $s = k \frac{a}{bw}$. The same cell was employed for both solutions so that any change in the cell constant or any error in its determination would be eliminated for comparison. Pairs of solutions were made which were isohydric with regard to each other and of a known molarity for an added salt. Three concentrations of each added salt were used. The specific conductivities of these solutions were now determined. When the conductivity of a solution, say molar with regard to potassium nitrate and half-molar with regard to sodium nitrate, had been measured, the cell was thoroughly

cleaned and dried. The same cell was now used for the determination of the conductivity of a solution .6984 molar with respect to calcium nitrate, that is, isohydric with potassium nitrate, and half-molar in regards to sodium nitrate. Thus possible errors were avoided.

The increase in conductivity of each isohydric solution was calculated for each added salt at every concentration and results are given in the third and fifth columns of each of the following tables. The difference between the increases for comparable solutions is found in the last column of each table. At the top of each table the concentrations of the two solutions which were isohydric are given.

In all cases the numbers given for conductivities are in Siemens units and represent the mean of at least three readings on the bridge for different resistances.

RESULTS

The headings in the tables which follow demand some explanation. The two main headings in each table are the concentrations of the two solutions which were made isohydric. s and s^1 are the specific conductivities of solutions, say for 111.78 in Table I, molar for KCl and eighth molar for NaCl. Δs and Δs^1 are the results obtained by subtracting from s and s^1 the specific conductivities of the corresponding isohydric solutions. $\Delta s - \Delta s^1$ is the difference in the increases Δs and Δs^1.

TABLE I.

Added Salt	V	Molar for KCl s	Δs	.695 M for $CaCl_2$. s^1	Δs^1	$\Delta s - \Delta s^1$
NaCl	8	111.78	8.18	100.57	7.45	0.73
NaCl	2	135.78	32.18	120.33	27.21	4.97
NaCl	1	162.09	58.49	142.67	49.55	8.94
KCl	8	115.38	11.78	103.35	10.23	1.55
KCl	2	148.75	45.15	132.56	39.44	5.71
KCl	1	191.68	88.08	169.98	76.86	11.22
NH_4Cl	8	115.30	11.70	103.25	10.13	1.57
NH_4Cl	2	148.25	44.65	132.06	38.84	5.81
NH_4Cl	1	190.14	86.54	169.98	76.86	9.68
$MgCl_2$	8	117.02	13.42	104.03	10.91	2.51
$MgCl_2$	2	148.11	44.51	131.38	38.26	6.25
$MgCl_2$	1	174.54	70.94	148.83	55.71	15.23
$CaCl_2$	8	118.97	15.37	105.73	12.61	21.76
$CaCl_2$	2	156.99	53.39	138.54	45.42	7.97
$CaCl_2$	1	192.64	89.04	167.16	74.04	15.00
$SrCl_2$	8	118.36	14.76	105.77	12.65	2.11
$SrCl_2$	2	156.28	52.68	137.22	44.10	8.58
$SrCl_2$	1	192.35	88.75	167.29	74.17	14.58

TABLE II.

Added Salt	V	Molar for NaCl s	Δs	.597 M for $CaCl_2$. s^1	Δs^1	$\Delta s - \Delta s^1$
NaCl	8	87.69	8.34	91.61	8.08	0.26
NaCl	2	110.79	31.44	112.61	29.08	2.36
NaCl	1	138.06	58.71	138.58	55.05	3.66
NH_4Cl	8	91.41	12.06	93.76	10.23	1.83
NH_4Cl	2	124.73	45.38	125.17	41.64	3.74
NH_4Cl	1	166.56	87.21	164.78	81.25	5.96
$MgCl_2$	8	92.24	12.89	95.16	11.63	1.26
$MgCl_2$	2	122.25	42.90	122.11	38.58	4.32
$MgCl_2$	1	148.18	68.83	145.29	61.76	7.07
$CaCl_2$	8	93.48	14.13	96.63	13.10	1.03
$CaCl_2$	2	130.05	50.70	130.51	46.98	3.72
$CaCl_2$	1	165.02	85.67	162.49	78.96	6.71
$SrCl_2$	8	93.88	14.53	97.05	13.52	1.01
$SrCl_2$	2	130.52	51.17	130.86	47.33	3.84
$SrCl_2$	1	165.46	86.11	103.69	80.16	5.95
KNO_3	8	89.08	9.73	92.35	8.82	0.91
KNO_3	2	115.32	35.97	115.26	31.73	4.24
KNO_3	1	147.11	67.76	142.34	58.81	8.95

TABLE III.

Added Salt	V	Molar for $NaNO_3$ s	Δs	.681 M for $Ca(NO_3)_2$. s^1	Δs^1	$\Delta s - \Delta s^1$
$NaNo_3$	8	76.92	6.82	78.58	5.70	1.12
$NaNO_3$	2	95.14	25.04	92.97	20.09	4.95
$NaNO_3$	1	116.09	45.99	109.79	36.91	9.08
KNO_3	8	78.54	8.44	79.89	7.01	1.43
KNO_3	2	102.38	32.28	99.19	26.31	5.97
KNO_3	1	129.99	59.89	122.10	49.22	10.67
NH_4NO_3	8	79.80	9.70	81.39	8.51	1.19
NH_4NO_3	2	107.34	37.24	105.18	32.30	4.94
NH_4NO_3	1	141.33	71.23	134.24	61.36	9.87
$Mg(NO_3)_2$	8	81.85	11.75	82.33	9.45	2.30
$Mg(NO_3)_2$	2	108.77	38.67	103.04	30.16	8.51
$Mg(NO_3)_2$	1	132.13	62.03	120.66	47.78	14.25
$Ca(NO_3)_2$	8	80.23	10.13	80.90	8.02	2.11
$Ca(NO_3)_2$	2	102.55	32.45	98.16	25.28	7.17
$Ca(NO_3)_2$	1	118.24	48.14	108.82	35.94	12.20
$Sr(NO_3)_2$	8	79.02	8.92	79.97	7.09	1.83
$Sr(NO_3)_2$	2	98.27	28.17	93.83	20.95	7.22
$Sr(NO_3)_2$	1	108.58	38.78	100.58	27.70	11.08
KCl	8	79.78	9.68	81.85	8.97	0.71
KCl	2	108.27	38.17	106.98	34.10	4.07
KCl	1	146.49	76.39	140.87	67.99	8.40

TABLE IV.

		.5 M for $NaNO_3$		.310 M for $Ca(NO_3)_2$.		
Added Salt	V	s	Δs	s^1	Δs^1	$\Delta s - \Delta s^1$
$NaNO_3$	8	76.92	6.82	78.58	5.70	1.12
$NaNO_3$	2	95.14	25.04	92.97	20.09	4.95
$NaNO_3$	1	116.09	45.99	109.79	36.91	9.08
KNO_3	8	78.54	8.44	79.89	7.01	1.43
KNO_3	2	102.38	32.28	99.19	26.31	5.97
KNO_3	1	129.99	59.89	122.10	49.22	10.67
NH_4NO_3	8	79.80	9.70	81.39	8.51	1.19
NH_4NO_3	2	107.34	37.24	105.18	32.30	4.94
NH_4NO_3	1	141.33	71.23	134.24	61.36	9.87
$Mg(NO_3)_2$	8	81.85	11.75	82.33	9.45	2.30
$Mg(NO_3)_2$	2	108.77	38.67	103.04	30.16	8.51
$Mg(NO_3)_2$	1	132.13	62.03	120.66	47.78	14.25
$Ca(NO_3)_2$	8	80.23	10.13	80.90	8.02	2.11
$Ca(NO_3)_2$	2	102.55	32.45	98.16	25.28	7.17
$Ca(NO_3)_2$	1	118.34	48.14	108.82	35.94	12.20
$Sr(NO_3)_2$	8	79.02	8.92	79.97	7.09	1.83
$Sr(NO_3)_2$	2	98.27	28.17	93.83	20.95	7.22
$Sr(NO_3)_2$	1	108.58	38.78	100.58	27.70	11.08
KCl	8	79.78	9.68	81.85	8.97	0.71
KCl	2	108.27	38.17	106.98	34.10	4.07
KCl	1	146.49	76.39	140.87	67.99	8.40

TABLE V.

	Molar for KNO_3			.698 M for $Ca(NO_3)_2$.		
Added Salt	V	s	Δs	s^1	Δs^1	$\Delta s - \Delta s^1$
$NaNO_3$	8	92.04	6.67	79.67	5.46	1.21
$NaNO_3$	2	109.73	24.36	93.91	19.70	4.66
$NaNO_3$	1	130.67	45.30	110.75	36.54	8.76
KNO_3	8	94.15	8.78	81.15	6.94	1.84
KNO_3	2	117.61	32.23	100.29	26.18	6.05
KNO_3	1	146.20	60.83	123.27	49.06	11.17
$Sr(NO_3)_2$	8	93.84	8.47	80.90	6.69	1.78
$Sr(NO_3)_2$	2	110.90	25.53	94.31	20.10	5.43
$Sr(NO_3)_2$	1	121.22	35.85	101.68	27.47	8.38
KCl	8	96.31	10.94	82.91	8.70	2.24
KCl	2	128.62	43.25	108.23	34.02	9.23
KCl	1	169.69	84.32	141.36	67.15	17.17
NaCl	8	94.15	8.78	80.98	6.77	2.01
NaCl	2	118.48	33.11	100.87	26.66	6.45
NaCl	1	146.90	61.53	123.94	49.73	11.80

DISCUSSION OF RESULTS

The conductivity values to be found in the second and fourth columns of the preceding tables are not the sums of the specific conductivities of the two salts present in each case, but are less than this sum because of the common ion effect. Furthermore, since the two solutions in any given case contain the same number of anions, the added salt not being considered, the driving back of the dissociation of the added salt by these anions, other things being equal, would be the same. An inspection of the tables will show that for every pair of solutions studied this suppression is more pronounced in the hydrated solutions. Or, stating it in another way, the increase in conductivity caused by the addition of the same amount of added salt is always greater in the non-hydrated solutions. This means that the added salts dissociate more in the last named solutions than in the comparable isohydric solutions of hydrated salts.

A closer inspection of the tables reveals the fact that the driving back of the ionization of the hydrated salts added is much greater than the driving back of comparable quantities of non-hydrated salts in both isohydric solutions of every pair studied.

Compare Tables III and IV. For any one added salt the difference in the increases of conductivity in Table III are approximately double the corresponding difference in Table IV. Finally, a few salts were added which do not have ions in common and these behaved in somewhat the same manner as the other added salts though the results are somewhat irregular. How can all these facts be explained?

A tentative explanation based upon these somewhat limited observations is offered which is by no means final. When a salt is added to water or to the solution of an-

other added salt, the added salt is dissociated by the water present. It is believed that combined water, i. e., water of hydration, in the solution of hydrated salts possesses less ionizing power than the uncombined water, in which case the salts added would be less dissociated. And further, this effect would be greater the greater the concentration since more combined water would then be present. The hydrated salts used as added salts are less dissociated than the other added salts because water of hydration now exists in both of any pair of solutions. However, the dissociation is always less in the case of the hydrated salt of any pair because of the less dissociating power of the water of hydration already present in that solution.

These results and conclusions which follow are to be regarded as preliminary. The nitrates and chlorides have been used and not the sulfates, principally because they are less liable to form double salts. But in the concentrated solutions it cannot be said with certainty that no complexes were present.

Values for the degree of dissociation based upon the equation, $\alpha = \frac{\mu}{\mu_\infty}$ are somewhat open to doubt.[17] The conductivity of a solution (apart from experimental errors) is dependent to a greater or less extent upon the viscosity of the medium and the migration velocity of the ions. The latest relation between viscosity and conductivity has been deduced by Washburn and Clark.[18] Unfortunately this is of little value in applying a viscosity correction, since one of the factors is dependent upon the nature of the medium and there is at present no means of evaluating it for solutions of strong electrolytes.

Considering the speed of the ions no quantitative cor-

17 J. Amer. Chem. Soc., **38**, 788 (1916).
18 J. Amer. Chem. Soc., **38** (1916).

rection can be made. It will be noticed that normal solutions of sodium and potassium nitrates have been paired with calcium nitrate solutions. The migration velocity of potassium is greater while that of sodium is less than the migration velocity of ½ calcium, yet this fact hardly affects the results. Lewis[19] has recently held that the speed of ions actually increases rather than decreases with increasing concentration, and so the degree of dissociation based upon the conductance ratio is always too high. The evidence either way, however, is not conclusive.

From his extensive work upon dielectric properties of solutions, Walden[20] concludes that the presence of salts in solutions increases the ionizing power of the solvent. With this granted then the hydrated salts may be said to alter the dielectric constant differently from the non-hydrated salts, since we believe their ionizing powers to be different. This does not mean that the combined water is more or less associated, for while the dissociating solvents with highest dielectric constants are usually most highly associated, the principle is not without exception.

The results presented here are relative. It would be interesting to make a further study along the same lines but eliminating any influence of viscosity by the use of some indifferent substance such as sucrose. Then, too, a determination of the dielectric constants of the various pairs of solutions by one of the methods suggested by Drude [21] or Smale[22] should lead one to a more definite statement.

19 J. Amer. Chem. Soc., **37,** 1043 (1915).
20 Zeit. physik. Chem., **55,** 683 (1906).
21 Wied. Ann., **59,** 17; **60,** 600.
22 Wied. Ann., **57,** 215; **60,** 625.

BIOGRAPHY

George Frederick Ordeman was born in Frederick, Maryland, on November 9, 1892. He graduated from the Frederick High School in 1909 and in 1912 completed the course in Mining Engineering at Washington and Lee University, Lexington, Va., receiving the degree of Bachelor of Science. In 1913 he received the same degree with "Special Attainments in Chemistry" at the same institution. In the summer of 1913 he attended the University of Wisconsin. During the academic year 1913-14 he was an Instructor in Chemistry at Washington and Lee. In the fall of 1914 he entered Johns Hopkins University as a graduate student in Chemistry with Physical Chemistry and Mineralogy as subordinate subjects. For the year 1914-15 he held a Hopkins Scholarship and for the year 1915-16 the Ilse Schmidt Fellowship.